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Progress in Pectin Based Hydrogels for Water Purification: Trends and Challenges

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ABSTRACT

Pectin is one of the finest natural polymer which has drawn great attention because of its applications in different fields. Due to the quintessential structure of pectin, it can be transformed into variety of useful products. It can be utilized as a blend in many polymers to make a mixture or a composite material. Owing to considerable collection in chemical conformation and cross-linking mechanism, different pectin based hydrogels have been prepared for different characteristics in pharmaceutical and bio-medical sites. Inventive properties of hydrogels like volubility, swellability, solvability and hydrophilicity make them better alternative for wastewater treatment. Recently, pectin based hydrogels have demonstrated excellent performance to eliminate various metal ions and dyes from the polluted water. The adsorption

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characteristics of pectin based hydrogels can be upgraded by using nanoparticles, which prompts to the development of hydrogel nano-composites. In this review article, we have summarized a comprehensive assessment in the direction of using pectin based hydrogels to remove toxic pollutants from aqueous solution. Sodium acrylate-co-N-isopropylacrylamide based pectin hydrogel has demonstrated the maximum adsorption capacities of 265.49, 137.43, 54.86, 53.86, 51.72 and 50.01 mg g^{-1} for the adsorption of methyl violet, methylene blue, Pb(II), Cu(II), Co(II) and Zn(II) respectively. We have also discussed the pectin structure, properties and applications in this article.

Keywords: Pectin; bio-waste material; pectin based hydrogel; water pollution; heavy metal ions and dye removal

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1. Introduction

Green chemistry gives an important requisite for sustainable addition to human society due to deteriorating environment (Hao et al., 2018; Kaveeshwar et al., 2018; Pakdel and Peighambardoust, 2018). It is also called defendable chemistry and used to diminish or remove toxic components from environment (Attallah et al., 2017; Raizada et al., 2017). In our environment, water pollution is the biggest global problem (Ji et al., 2018). Water pollution adversely affects many living organisms creating serious health related issues (Baciak et al., 2016). Hydrogels can find useful applications in water purification because of their specific properties (Ali et al., 2012; Dudu et al., 2015; Li et al., 2017) **(Figure 1)**. Hydrogels are branched polymers with three dimensional structures having excellent water absorption capacity (Bian et

al., 2018; Li et al., 2017). Hydrogels can be represented as the binary system of any significant polymer and fluid in which the development of sol happens when the collaboration is very supported in polymer-fluid than that of both polymer-polymer interactions and liquid-liquid interactions (Amini and Nair, 2012; Chenite et al., 2000; Tous et al., 2011; Zhang et al., 2013). Super absorption properties of hydrogels are sensualized to their capability to absorb maximum volume of liquid or water (Shahmirzadi et al., 2018; Shin et al., 2009a, 2009b; Wang et al., 2017), approximately 10 to 20 times to the actual weight (molecular weight) of hydrogel and after absorption of liquid or water, the hydrogel occupy swollen form (Fang et al., 2016; Kim et al., 1992). The applications of hydrogel like pliability, flexibleness, stretchiness and porousness are sensualized to the water absorption ability (Ji et al., 2018; Thakur and Arotiba, n.d.). Hydrogels exhibits both partially liquid and fully solid characteristics (Jagur-Grodzinski, 2010; Zhao et al., 2015a). A three dimensional configuration of hydrogel is normally originated via physical and organic/chemical cross-linking (Khan et al., 2016; Pereira et al., 2011). The major liable characteristics for the production of physically crosslinked hydrogel are (a) electrostatic interactions (b) hydrophobic interactions (Steed, 2011) (c) co-ordination bonds and (d) hydrogen bonding (Appel et al., 2015). The amphiphilic chemical/organic molecules (Liu et al., 2011) or inorganic nano-composites in the form of aqueous solution are able to produce hydrogels with super-molecular chemistry (Pakulska et al., 2012). On other hand, there are some changes in around positional circumstances in chemically reacted hydrogels (Adesanya et al., 2014; N. Thakur et al., 2018a) like (a) pH (Barrett et al., 2013) (b) ionic strength (Zhao et al., 2015b) (c) temperature (Thakur et al., 2015; Xia et al., 2013) and (d) electric field (Parisi-Amon et al., 2013) which shows the quantity phase isomerization (Yoshimura et al., 2005). Hydrogels have a permeable nature which allow them to the retention of waste/poisons/pollutants from the

polluted/waste water (Thakur et al., 2018b; Peppas, 2010). The production of hydrogels have been raised because of their excellent absorptive behavior (Buchholz and Graham, 1998; Hogan, 2010; 2013; Peppas and Khare, 1993; Rosiak and Yoshii, 1999; Teshager et al., 2016; Wandrey et al., 2010). Durable and degradation properties are the major advantages of biopolymer hydrogels (Adsul et al., 2016). If polymers are hydrophilic and water used as liquid, then the product formation with strong polymer-liquid interactions are known as hydrosols. The limits of the reaction are mainly dependent upon the various kinds of functional groups, polymer structures and the amount of ions in polymer structure as well as the final solution, pH and temperature. The solution of a hydrophilic polymer in the water as a fluid can be stopped by the expansion of cross linkers by utilizing either physical or by chemical process and these crosslinked hydrosols are called hydrogels (Fang et al., 2016; Thakur and Thakur, 2014; Thakur and Voicu, 2016). They can swell just in the surrounding fluid to a specific swelling proportion dependent on the concentration of used cross linkers.

Hydrogels have specific properties like excellent absorptive behavior to deal with polluted water. Hydrogels are the three-dimensional network chain polymer that are hydrophilic in nature, insoluble in water, sometimes found like a colloidal gel and water behave as dispersion medium (Buchholz and Graham, 1998; Li et al., 2013; Peppas and Khare, 1993; Thakur et al., 2017). These are also crosslinked polymer chains that soaks up tolerable quantity of water or any aqueous solution (Thakur et al., 2018c). The network chains are possessed by the homo-polymers or co-polymers and are unsolvable due to the existence of chemical crosslink (Bae et al., 2015; Li et al., 2014; Ren et al., 2014; Singh and Singh, 2012; Wichterle and Lim, 1960) (tie–points, junctions) or physical crosslink, such as involvement or crystallization. The huge volume of water constituents of materials contributes to their bio-compatibility (Rosiak and

Yoshii, 1999). The double cross linking gives the network chain structure and physical rawness. Hydrogels possess thermodynamic characteristics with water which permit them to swell in the given medium. Hydrogels contains very huge amount of water i.e., over 90 % of water and are known as good natural absorbent (Rosiak and Yoshii, 1999). They also possess degree of flexibility similar to the earthy tissues due to the expressive water content. The stimuli responded swelling hydrogels are the environmentally friendly, have the great ability to respond the changes in their superficial environment (Ferry, 1980; Wach et al., 2002). They exhibit some complicated substitutes in their swelling properties, network chain structure and unconscious intensity in response to the changes in ionic strength or pH of the surrounding biological fluid or temperature. Due to their nature, these substances shows various applications in a broad spectra, like separation membrane, chemical valves and some drug delivery devices, etc. (Ahmed, 2015). Mechanism of network formation; gelation deals with the connecting of macro-molecular catena together which originally over to the successively weightier branched; up to now soluble polymer depend up on the structure and formation of the starting constituents/components **(Figure 2)**. The composites of such poly-disperse bifid polymers are known as ‘sol’ (Gulrez et al., 2011). In other words, this ‘eternal polymer’ is named as ‘gel’ or ‘circuitry’ and is infiltrated with outspread polymers. The conversions from a complex with definable stretched polymer to interminable molecules are known as ‘sol-gel conversion’ (or ‘gelation’) and the analytical point where gel generally appears known as the ‘gel point’ (Bajpai et al., 2008; Ben-Nissan et al., 2016). Gelation can appear either by physical coupling/linking or by chemical coupling/ linking (Gulrez et al., 2011).

Some common elements include polyvinylalcohol (PVA), sodium poly-acrylate, acrylate-polymers and various copolymers with the richness of water loving groups. These polymers

exhibit a common property of being capable to take up the huge amount of water (Bajpai et al., 2008). In physical gels, the character of the crosslinking action is physical. This is generally accomplished by utilizing physical actions like coalition, aggregation, affiliation, crystallization, complication and hydrogen bonding (Gulrez et al., 2011). Conversely, a chemical process in which synthesized bivalent crosslinking is idolized to assemble a chemical hydrogel with superior properties. Physical hydrogels are convertible/reversible in nature due to the informational additions and chemically cross linked hydrogels are unchangeable/permanent in nature. More information about the hydrogels is shown in **Table 1**. Responsive hydrogels can be categorized into various forms in response to alteration in environmental factors such as pH, temperature, and liquid composition which partially depends upon its structure. Hydrogels can counter to environmental alterations via reforming their size or shape as presented in **Table 2** (Huang et al., 2004). Most dominant characteristics that activate hydrogels are pH, temperature, and swelling medium. While for the term non-ionic hydrogels are practically inconsiderate to pH selection, ionic hydrogels indicates generous/sensible differences in size with some modification in pH. Until the point that the temperature is troubled, hydrogels require hydrophobic compilations or those influences the chain collection counter to the temperature modification in extensive scale (Satarkar and Hilt, 2008).

Actually the appearance of solvability and swellability/volubility are directed by alike physical energies, the reaction of the hydrogel to the temperature variations are either constant or not. As a result, the solvability and volubility of the hydrogel can increase with increase in temperature, conversely checked with reverse thermo-responsive hydrogels. Hydrogels can also alter their size and shape with the change in constituents of the swelling standard solution. Opulently, the hydrogel reactions would be effective if the swelling medium occupies salt and a non-solvent.

Number of applications of pectin based materials have been explored in the literature due to its lavishing characteristics (Mohnen, 2008).

Sepehri and Sarrafzadeh both examined the membrane polluted in membrane bioreactors and found that it usually depends on the microbial occupant's structure and microbial cell solidity. A nitrifying-enriched activated sludge occurred in this examination during particular ammonium nourishing of conventional activated sludge. Next, the predominance of autotrophic nitrifier population in nitrifying-enriched activated sludge scheme was checked and evaluated with conventional activated sludge scheme by its excellent nitrification efficiency (100% vs. 43%) and low chemical oxygen demand exclusion (9% vs. 65%). Furthermore, the greatest quantity of N-NO^{3-}formed from same concentrations of ammonium in conventional activated sludge and nitrifying-enriched activated sludge schemes were 6.6 mg L^{-1} and 37.5 mg L^{-1} respectively (Sepehri and Sarrafzadeh, 2018). In this article, we will discuss about the potential of bio-waste pectin for water treatment along with its structure and properties. The pectin based hydrogels for water purification has been primarily reviewed in present article.

2. Pectin

2.1. Pectin from bio-waste materials

This part of the article will focus on explaining the effect of the bio-mass resources on the structural characteristics which are representative of pectin-rich biomass, for examples: mango, guava, and waste apples etc. The bio-wastes are examined in numerous investigations which are an industrial waste produced in fruit waste materials like orange, apple, mango peels and so on **(Table 3)**. The fruits peel waste after juicing is effectively and abundantly obtained as a low quality by-product. Researchers have examined the adsorptive migration of arsenic by consuming a metal-stacked gel synthesized from orange fruit waste (Ghimire et al., 2002). An

orange waste composite occupies around 10 % pectin which prevails in the cell wall as an intercellular creating material. Pectin is a natural polysaccharide material in which pectic acid and some acidic polysaccharide units are partly esterified through methyl groups (Banerjee et al., 2016; Fidalgo et al., 2016). It is easily changed into pectic acid through saponification with alkali groups like calcium hydroxide. In the past work, it was shown that pectic acid and alginic acid firmly connected with different heavy metals contributing to stable five member ring chelates (Dhakal et al., 2005). **Figure 3** represent brief schematic on extraction of fruit waste material as a pectin powder.

2.2. Structure

The pectin is hetero-polysaccharide found in essential cell walls of terrestrial/earthy plants (Yapo, 2009). Pectin's were reported first via Henri Braconnot in 1825 (Yapo, 2010, 2011). It is procured in commercial form mostly in light brown color and is mostly made by citrus fruits, and most of the food is used as a jelling agent, mostly in jelly and jam. Pectin was introduced to the foundation in 1825 via Henri Braconnot (Yapo, 2010, 2011), while the method of marmalade and jam was being used by pectin already. To make good accumulated jam with fruit, mostly bad pectin or other low-pectin fruits were added to the process. At the time of the Industrial alteration, it was made in liquid form. After that, pectin was made and used in powder form since the years of 1920 and 1930. It is very easy to utilize and handle the powder form (Ahlawat et al., 2007). In plant biology, there is a strong group of polysaccharides in pectin, which is found in the walls of most beginning cells as shown in **Figure 4** (Lodish et al., 2008). It is found in excessive amounts in non-wooded part of terrestrial/earthy plants. Pectin is most valuable constituent of middle lamella, where it supports to keep cells together, but it also exist in the wall of the beginning. The amount of pectin and chemical structures are found separately in every

portion of plant. Pectin is one of the important cell wall polysaccharides extending the starting cell wall and commands the plant to grow. At the time of fruit maturation, pectin is damaged by enzyme pectinase and pectinestraes. In this biological activity, the fruits become soft (Grierson et al., 1986) and pectin gives the property of a kind of soluble fiber (Huang et al., 2007; Lindinger et al., 1997). Pectin in fruits and vegetables is present in the form of poly-molecular and poly-disperse form in relation to its chemical constitution and molecular density (Mohnen, 2008b). The statistical and percentage data of monomeric units of pectin may vary for various materials that further depend upon the origin, the protocol used for isolation and subsequent analysis. Different physical and chemical characteristics of pectin can be utilized for preparing its various forms based on origin and isolation method (Laurent and Boulenguer, 2003). Pectin is a polymer of rhamnogalacturonan-1 (RG-1). The basic point and main character of all pectin fragment is a single chain of (1+4)-linked a-D-galactopyranosyluronic acid groups, forming it a-D-galacturonan. Approximately "all earthy pectin's" few carboxyl units are in the form of methyl ester (Yapo, 2011). Based on the conditions of isolation, the rest of free carboxylic acid units may be half or fully neutralized, i.e., half or fully commenced as Na, K or ammonium acetate groups. The relative density of partially esterifies sugar acid unit to complete sugar acid groups is "Traversed the quality of esterification" (Ridley et al., 2001) and strongly effects the solvability, capability to make gel, circumstances required for the gelation, gelling temperature and gel characteristics for the synthesis (Mesbahi et al., 2005). In pectin from origins, few groups occur as 0-2 or 0-3 acetates. All pectic polysaccharides are to a definite extent O-acetylated. The acetyl-moieties are frequently involved to the 0-2 and 0-3 locations of the galacturonic acid moiety of mutually homogalacturonic (HG) and RG-I. Acetylation of the pectin affects the gelation characteristicsof this category of the polymers, which is significant for the food

production industries. The acetate groups might unnecessarily interfere among the calcium crosslinking among HG polymers by the use of steric hindrance. Such compounds change to ester that prevents the gel formation, when one sugar acid unit out of eight sugar acid groups is mono-esterified by 0-2 or 0-3 acetates (Kirby et al., 2006). The occurrence of acetyl groups, hence, forms some potential origins of commercial pectin, e.g., (round red root vegetables) sugar beet (Amaranth, spinach etc.), sunflower, fruits waste (orange, mango, banana etc. fruit peels) and potato (less desirable). Neutral sugars, primarily L-rhamnose also occur, however, the disunity over the arrangement in the bilinear chain (Leroux et al., 2003). As present in **Figure 5**, structure of pectin shows three different pectic polysaccharides i.e. homo-galacturonan, rhamnogalacturonan (RG-I) and rhamnogalacturonan II (RG-II) attached with each other (Mohnen, 2008a; Minzanova et al., 2018). Pectic polysaccharides can be presented by three different parts (Caffall and Mohnen, 2009; Ovodov, 2009; Pedrolli et al., 2009; Ridley et al., 2001b) (Valdés García et al., 2015) **(Figure 6)**. **Figure 6** demonstrates the classification of pectic polysaccharides on the bases of D-galacturonic acid (Valdés García et al., 2015).

2.3. Physical properties

Pectin is a group of substances which forms gels when dissolved in water under suitable conditions. It is derived from the protopectin found in the middle lamellae of plant cells. Protopectin is insoluble, but is converted to soluble pectin as fruit ripens. If dissolved at a high temperature, mono-valent diazonium salts or alkali metal salts of pectic acids are normally solvable only in water but not in case of any liquids; di-valent and tri-valent diazonium salts are weakly solvable or insolvable (BeMiller, 1986). However, pectin is not taken as thickening agents; pectin mediums acquire the non-Newtonian, Pseudo plastic properties of many poly-saccharides. With solvability, density of pectin solution is connected to molecular/atomic weight,

degree of esterification (DE), concentration of the synthesized solution, the pH behavior and occurrence of ions in prepared solution (Evageliou et al., 2000). Normally density, viscosity, solvability and gel formation are correlated, i.e., parameters that increases the volume of gel, for example, will rise the capacity to gel, lower solvability, and raise density/viscosity (Brigand et al., 1990). All these physical characteristics of pectin are due to their configuration which is a bi-linear poly-anion (poly-carboxylate) (Plaschina et al., 1978).

Three different methods are usually planned for the accomplishment of alkalinity enzymatic alteration of polysaccharides: (i) single-chain method, whereby the necessary of the enzyme is followed via exchange of all neighboring substrate positions on the polymer chain; (ii) multiple-chain method, whereby the enzyme-substrate compound separates subsequent to every reaction, resultant in the alteration of a particular residue for every attack; and (iii) multiple-attack method, whereby the enzyme catalyzes the alteration of a restricted usual quantity of residues for each dynamic enzyme-substrate compound produced. The usual number of developed residues has been defined as the degree of multiple attacks (Duvetter and Fraeye, 2006).

Duvetter and Fraeye examined the mode of de-esterification of alkaline and acidic pectin methyl esterase at different pH conditions. Extremely esterified citrus pectin was de-esterified at pH 4.5 and 8.0 through a fungal pectin methyl esterase. Interchain de-esterification pattern was calculated by absorption of the pectin products with endo-poly-galacturonase and successive study via size elimination and anion exchange chromatography. No effect of pH was seen on the de-esterification method of both of the two proteins. Acidic, parasitic pectin methyl esterase changed over pectin as indicated by different chain methods, with a restricted level of various multiple attacks at the intra-chain level, both at pH 4.5 and at pH 8.0. A multiple-attack method, with a high level of multiple attacks, was increasingly suitable to represent the activity mode of

alkaline, plant pectin methyl esterase, both at pH 4.5 and at pH 8.0 (Duvetter and Fraeye, 2006). **Figure 7** presents the combination arrangement of a pectenic acid of DE (degree of esterification) with the alkaline de-polymerization (BeMiller, 1986)**.**

2.4. Chemical properties

The dissolved pectin undergoes depolymerization in aquatic systems. The greatest stability of pectin is at pH 4. Below and above this pH, de-esterification of pectin occurs resulting in its decreased stability. De-ionification rate is higher than the rate of depolymerization. The presence of solvents, which reduces water activity, reduces the rate of both reactions. Depolymerization occurs through the acid catalyst hydrolysis of glycosidic bonds at low pH values. Acid-activated hydrolysis is preferentially on L-rhamnopyranosyl glycosidic bonds (BeMiller, 1967). The galacturonanglycan chain is formed in hydrolysis of these links, which occur with polymerisation of approximately 25 (Powell et al., 1982; Thibault et al., 1993) side chain, especially with L-arabinofuranosyl unit. However, if the side catena are attached to rhamnogalacturonan sequence (Guillon et al., 1989), the conversion to smooth surface is not possible with acid treatment as the depolymerization of L-hamnopyanosyl bonds occurs at pH 5-6 (BeMiller, 1967). Beta-eradication reaction of pectin chains, a reaction which is stimulated by organic ions, it is the erosion of beta-eradication de-polymerisation reaction, which is only in monosaccharide units esterifies by the indigestion of pectin. From 6 to the upper pH values, both de-esterification and de-polymerization reaction proceed and there is also a rapid response at atmospheric temperature (Schneider and Fritschi, 1936; BeMiller, 1986; Vollmert, 1949; Whistler and BeMiller, 1958; Albersheim, 1959; LAUNER and TOMIMATSU, 1961). **Figure 8** presents the repeating unit of functional groups; COOH (carboxylic group), ester group and also presents amide group ($-NH_2$) in the frame of pectin chemical structure. All these groups are

attached in pectin chain (Sriamornsak, 2003). **Figure 9** demonstrates the schematic presentation of rhamnose insertion cause occurrence of galacturonic acid (GA) chain, where S represents the occurrence of neutral sugar (Sriamornsak, 2002, 2003).

The termination of carboxyl (COOH) group in hydroxyethyl groups has been carried out with diborane (Smith and Stephen, 1960). It has also been found with hydroxyethyl and methyl ester (Haaland, 1972). Reducing carboxyl groups with water soluble carbodiimides have been easily activated (BeMiller, 1986b). When ammonia (BeMiller, 1986) is used to make modified low methoxyl pectin from us-pectin, some methyl carboxylate groups are converted to carbon (C) group, in which modified pectin is produced. In the presence of amide ($-NH_2$) group, the molecule becomes less hydrophilic, the tendency of pectin gel increases and sensitivity to calcium ions decreases (Deuel and Neukom, 1947).

Generally there are several types of such isomerase that actions on pectin molecules (BeMiller, 1986). Those enzymes produced by high plants have played an useful role in the reactions, resulting in crust in fruits or vegetables, and the textual changes occurring during processing (Bourne, 1989). The use of fungal enzyme by the fruit vitality industries increases the clarity of the juice. Control of their operation is crucial for formation of pectin. Pectin esteraes induce hydrolysis of methyl ester groups and they are usually undesirable for commercial uses (McFeeters and Lovdal, 1987). However, some fungal pectinsteraes produce lm-pectins, which are similar to that of pectins, which have the ability to gel with bases and acids and de-esterifies with sensitivity to calcium ions. Fungal pectinesteraes from Aspergillus japonicas is capable to exchange high methoxyl (hm) pectin into low methoxyl (lm) pectin able of producing strong gels with calcium ions. Pectinesterase quickly changes high methoxyl pectin into low methoxyl pectin below gentle situations with no de-polymerization of pectin particles. However, low

methoxyl pectins formed by pectinesteraes (ELM-pectin) have been originated to the appearance of weaker gels than those formed via extra techniques due to the non-random sharing of methoxyl groups amongst particles of the pectin (Ishi et al., 2006). All act as a beta eradication reaction for elevation, such as during base-induced depolymerization. The rate of depolymerization is proportional to the degree of esterification (DE) and suggests a requirement for a non-certified D-galacturonic acid unit (McFeeters and Lovdal, 1987).

2.5. Pectin gelation

Under acceptable circumstances, pectin poly-saccharides are capable of forming the gels, irrespective of the useful groups such as amide, methyl, carboxyl, acetyl and hydroxyl exist on the polymer. The method of branch establishment is totally dependent upon the class of functional group. Although the gel characteristics are resolved via the microscopic arrangements of pectin and gel constitutions (Evageliou et al., 2000, 2005). It means the use of pectin can give products a formation of contributing network, thereby changing few physical applications and chemical strength of (emulsifiers) emulsion-based edible materials. While normally the network formation of emulsified oil results in establishment of network (Leroux et al., 2003). Hence, jelly inconstancy, in emulsion-based edible material, the non-adsorbed pectin might form crystalline polymer material to which oil drops are captured (dispersed).

Gelation of pectin arises in alkaline situations through KOH or NaOH in a concentration and time dependent approach. Bernhard Wehr et al. suggested that alkaline environment show the way to de-methoxylation of pectin and make complete dissociation of carboxyl group units. Dissociation of carboxyl group outcome is highest revulsion of the pectin networks which must prevent gelation. As gelation happens, it has to be accomplished that K and Na ions neutralize the negative charge of pectin. As high concentrations of K or Na ions are essential to make

gelation, these ions also results in shielding of the carboxyl groups, thus assisting gelation. This can also be realized from the study that the Na–pectin gels liquefy in the lead of broad dialysis. This marks to a mutual charge neutralization and ionic strength achieved on the mono-valent cation-produced gelation of pectin (Bernhard Wehr et al., 2004).

3. Pectin based hydrogels for water purification

Different kinds of pectin based hydrogels have been utilized to eliminate pollutants from aqueous solution (Chauhan et al., 2007; Fares et al., 2011; Guilherme et al., 2010; Kumar et al., 2009; Singha et al., 2017). **(Table 4)**. Recently, Singh et al., synthesized interpenetrating polymer network super adsorbent (IPNS) pectin-g-(sodium acrylate-co-N-isopropylacylamide) (PC-g-(SA-co-NIPA)) hydrogel, sodium acrylate (SA) as monomer and N,N'-methylene-bis-acrylamide as cross-linker (Singha et al., 2017). The synthesized hydrogel was used for the adsorption of dyes and metal ions from aqueous solution. Pectin-g-(sodium acrylate-co-N-iso-propylacylamide) hydrogel was synthesized via cross linking of sodiumacrylate (monomer) using free radical polymerization reaction. Potassium per-sulfate (PPS) and sodium bisulfite (SBS) were used in the reaction as a redox pair initiator under specific nitrogen (N_2) atmosphere for the initiation of polymerization reaction **(Figure 10)**. The peaks at 2θ = 12.00°/13.35°/19.38°/25.29°/38.82°/40.60° and 23.48°/32.02°, corresponded to PC and SA-co-NIPA (Mishra et al., 2008; Sharma and Ahuja, 2011) respectively **(Figure 11a and inset)**. The peaks at 25.39, 27.07 and 31.83 corresponded to MB whereas peaks at 22.82, 31.96 and 45.78 ascribed to MV **(inset of Figure 11a)**. The peak at 2θ = 21.23°, assigned to IPNS **(Figure 11a)**. The increase in crystallinity after the dye adsorption was attributed to well order of dye packing at surface of IPNS (Singha et al., 2013) **(Figure 11a)**. The intensities of metal ions adsorbed IPNS hydrogel were increased in the order: Pb (II) <Zn (II) <Cu (II) <Co (II) **(Figure 11b)**. The

broad spectrum of IPNS–Pb (II) was due to the formation of different geometries (hemi). The intense peak of IPNS–Cu (II) was due to lesser number of equal arrangements. As compared to sodium acrylate-co-N-isopropyl acrylamide (SA-co-NIPA), interpenetrating polymer network superabsorbent (IPNS) showed rougher surface indicating high phase mixing of the polymeric chain in IPNS **(Figure 11c, d)**. Phase domains of SA-co-NIPA were clearly distinguishable; however phase boundaries were missing in case of IPNS due to the high cross-linking of chains. Adsorption of M (II), on the decided surface zone of IPNS, was distinguished from the predominant characteristics peaks of respectively EDX spectra **(Figure 11i-l)**. Among the M(II) consumed IPNS, Cu^{2+} were seen to store as greater crystals over the whole IPNS surface **(Figure 11f)**, and were also approved from the sharp and intense peak in **XRD (Figure 11b)**.In the IPNS-Zn^{2+} (**Figure 11g)**,the surface population of larger crystals appeared to be generally lower than IPNS-Cu^{2+}, additionally confirmed from the respective XRD spectra **(Figure 11b)**. On the other hand, similarly lesser amount of Pb^{2+} crystal of low dimension, at the IPNS surface **(Figure 11h)**, overstated the presence of characteristic low intensity XRD peak of IPNS-Pb^{2+} (**Figure 11b)**. Interestingly, surface statement of Co^{2+} crystal was the minimum **(Figure 11e)**, additionally caught from the expansive amorphous nature of the XRD range **(Figure 11b)**.

In another work, the biosorption and desorption processes were reported for Cd^{2+} ion from aqueous solution by using polyacrylic acid grafted pectin hydrogel (Fares et al., 2011). **Figure 12** present the reaction mechanism for polyacrylic acid grafted pectin hydrogel by using acrylic acid (AA) as a monomer and glutaraldehyde (GA) as cross-linker. In this mechanism, the pectin was treated with ceric ammonium nitrate to facilitate the formation of free radicals onto the pectins moiety. Prominently electrostatic interactions were involved in the formation of polyacrylic acid grafted pectin hydrogel. **Figure 13** shows the SEM images of pure pectin and

polyacrylic acid grafted pectin hydrogel with different magnifications. Pure pectin has been found in the form of flakes having highly agglomerated structure. However, upon grafting of acrylic acid onto pectin, due to the interaction between pectin and polyacrylic acid moieties, the sheet becomes more flattened. Grafting helped in the formation of two dimensional sheet like structure having thermally stable pectin moiety (Fares et al., 2011). The process of Cd^{2+} ion adsorption was experimentally described on the basis of pseudo 2^{nd} order kinetics. **Figure 14** show the ^{1}H-NMR result for polyacrylic acid grafted pectin hydrogel, the adsorption peaks at δ= 1.831 and δ=3.814 were due to polyacrylic acid and CH_2 respectively. The CH_2 peak of polyacrylic acid was found at δ value of 1.661, 1.831 and 3.841 ppm. However, the COOH moiety peak was observed at δ=11.75 ppm and for CH moiety peaks were allocated at δ = 2.5 and 2.702 ppm. The different position of protons having different environment exhibited numerous chemical shift as observed in case of pectin moiety at δ= 3.275, 3.589 and 4.483 ppm. Naushad et al. synthesized pectin based anion exchanger material to remove phosphate anions from aqueous solution (Naushad et al., 2018). At 55^{o}C, the maximum phosphate uptakewas75 %. The occurrence of little intensity peaks indicated semi-crystalline behavior of pectin based quaternary amino anion exchanger (Pc-QAE) material **(Figure 15)**. **Figure 16** present the SEM morphology of pectin based quaternary amino anion exchanger (Pc-QAE) material at different magnifying scales which showed the irregular and rough morphology of the fabricated pectin based quaternary amino anion exchange material (Naushad et al., 2018).

Reddy et al. synthesized pH sensitive semi-IPN pectin/poly(acrylamide-co-acrylamidoglycolic acid) (PPAA), hydrogel for the adsorption of Cu^{2+} and Ni^{2+} ions (Reddy et al., 2016). The most extreme adsorption limits of 203.7 mg g^{-1} and 121.7 mg g^{-1} were accounted for Cu^{2+} and Ni^{2+} ions respectively. The FTIR spectra of PPAA semi-IPN hydrogel showed a strong amide band at

1,656 cm^{-1} which appeared usual for the C=O broadening vibrations of the amide units. A wide and combined band at 3,000– 3,400 cm^{-1} demonstrated –OH and –NH stretching. In case of Cu^{2+} stacked hydrogels, the intensities of all peaks winded up higher than PPAA hydrogels and furthermore the peak of amide band moved from 1,656 to 1,662 $cm^{-1}$and peaks at 1,407 cm^{-1} moved to 1,413 cm^{-1}. This was due to direct result of incredible measure of Cu^{2+} in the PPAA semi-IPN hydrogels. Where as in the case of Ni^{2+} stacked hydrogel, there was a little increment in the intensities of peak at 1,407 cm^{-1}, which was due to smaller amount of Ni^{2+} in the PPAA semi-IPN hydrogel. This revealed that semi-IPN hydrogels had higher adsorption limit with Cu^{2+} ion than the Ni^{2+} ion (Reddy et al., 2016). Lessa et al. prepared pectin/cellulose microfibers composite beads for the removal of multi-metals from the aqueous medium (Lessa et al., 2017). Reported adsorption capacities of Cd^{2+}, Cu^{2+} and Fe^{2+} ions were 192.3, 88.5 and 98.0 mgg^{-1} respectively. Pectin cellulose microfibers (Pec-CF) beads demonstrated an irregular and porous surface with high roughness. After the adsorption, the surface of the beads turned out to be less rough. Moreover, the vacant spaces at surface reduced with respect to unexposed beads. Such more regular and compact morphology resulted because of the interactions between the divalent metals and Pec-CF. The acidic treatment in the metal desorption influenced the bead morphology. The beads surface indicated high roughness and irregular outlook similar to that observed for the unexposed beads. However, regenerated beads demonstrated tiny pores that led to decreased adsorption limit. Modified-pectin-co-acrylamide-co-acrylic (M-Pec-co-AAm-co-AAc) hydrogel was prepared and utilized for the removal of $Cu^{2+}$and Pb^{2+}ions from aqueous solution (Guilherme et al., 2010). The adsorption tendency of 120 and 130 mg g^{-1} were obtained for $Cu^{2+}$and Pb^{2+} ion respectively. Adsorptions studies were achieved for Cu^{2+} and Pb^{2+} ions through batch method with concentration of 0.10-0.05 g ml^{-1}. The minimum swelling was

reported at 0.10 g ml^{-1}, while maximum swelling was observed at 0.05 g ml^{-1} (Guilherme et al., 2010). Kumar et al. performed experiments to remove As (V) ions from the polluted water/water using iron (II) loaded pectin based hydrogel. Iron (II) loaded pectin based hydrogel was synthesized in the presence of 2-acrylamido-2-methylpropane sulphonic acid (Kumar et al., 2009). Three types of pectin and acrylamide supported hydrogels were formed to eliminate cationic/anionic ions from the water. The list of synthesized hydrogels (Chauhan et al., 2007): (i) pectin-cl-poly-acrylamide hydrogel, (ii) pectin-cl-poly-N-isopropyl-acrylamide hydrogel and (iii) pectin-cl-poly-2-acrylamido-2-methyl-1-propane-sulfonic hydrogel. These synthesized hydrogels were utilized to eliminate Cr^{6+}, Cu^{2+} and Fe^{2+} ions from the waste water or water. These hydrogels were reported with excellent sorption result for $Cr^{6+,}$ Cu^{2+} and Fe^{2+} ions (Chauhan et al., 2007).

At present, waste water is one of the most significant challenge that we are facing in our society. Sustainable and low-cost contribution of clean water to the society is essential for universal prosperity and health. In this direction, adsorption related skills and expertise will most probably play an essential role in water remediation due to both cost-effectiveness and energy-efficiency. To accomplish this, pectin based hydrogels are the most proficient alternatives to the foreseeable sorbents for eliminating main contaminants from waste water; like dyes, pesticides and heavy metal ions etc from water. A new opportunity can be opened for cracking the environmental harms through the natural polymer based hydrogels for heavy-metal and dye adsorption to preserve collective sustainable improvement. The future of pectin based hydrogels in water remediation is bright, however it needs the mutual efforts of both non-government and government regions to expand some sustainable and scale-up modern approaches to supply clean water to the society. There are numerous requirements of pectin based hydrogels for water

treatment: (i) new categories of pectin based hydrogels with cheaper raw materials; (ii) improving the mechanical properties of pectin based hydrogels and (iii) functionalization of pectin based hydrogels to synthesise through ecologically approaches.

To summarize, in spite of significant interest in pectin-based hydrogels, the current technologies available for their efficient use are quite limited. So research community around the globe should explore a number of innovative strategies for the effective and efficient use of pectin based hydrogels for water treatment.

4. Conclusion and future directions

Naturally occurring polymers are of essential significance amid which pectin occupies different arrangement for its effortless accessibility, non-hazardous and eco-friendly nature. Pectin and its compounds are prepared with various chemical and physical properties. Pectin attains its complete thickness even in cold water different from other polymers that need constant hot water treatment for accomplishing the similar thickness. It can be mixed together with other polymers like karaya gum, gelatin, xanthan gum and other cellulosic polymers to attain synergistic thickness product. The increasing acceptance of this polymer is supported by its non-poisonous and ecological nature. The methods of forming pectin-based materials for different kinds of applications and number of published articles with characterization results are constantly increasing. In case of pectin, the number of published articles on natural bio-polymers is high, however, there is limited work done on usage of pectin based hydrogels for water purification. There are many reasons for this; as it has been found according to its non-poisoning and low cost, it gives different gelling capacities due to differential size and differentiation in chemical structure from different sources. To increase interest in pectin based content, technology can be improved for the product of pectin. The mechanical strength and the adsorption efficiency of

pectin based hydrogels can be upgraded via integrating inorganic fillers into the matrix. Pectin and pectin based materials have a very high potential to play an important role indifferent fields. In pharmaceuticals, it can be used as emulsifying, suspending, stabilizing and binding agent for predictable dose form. In tablet or capsule dose form, it can be used as a disintegrating and potential binding agent.

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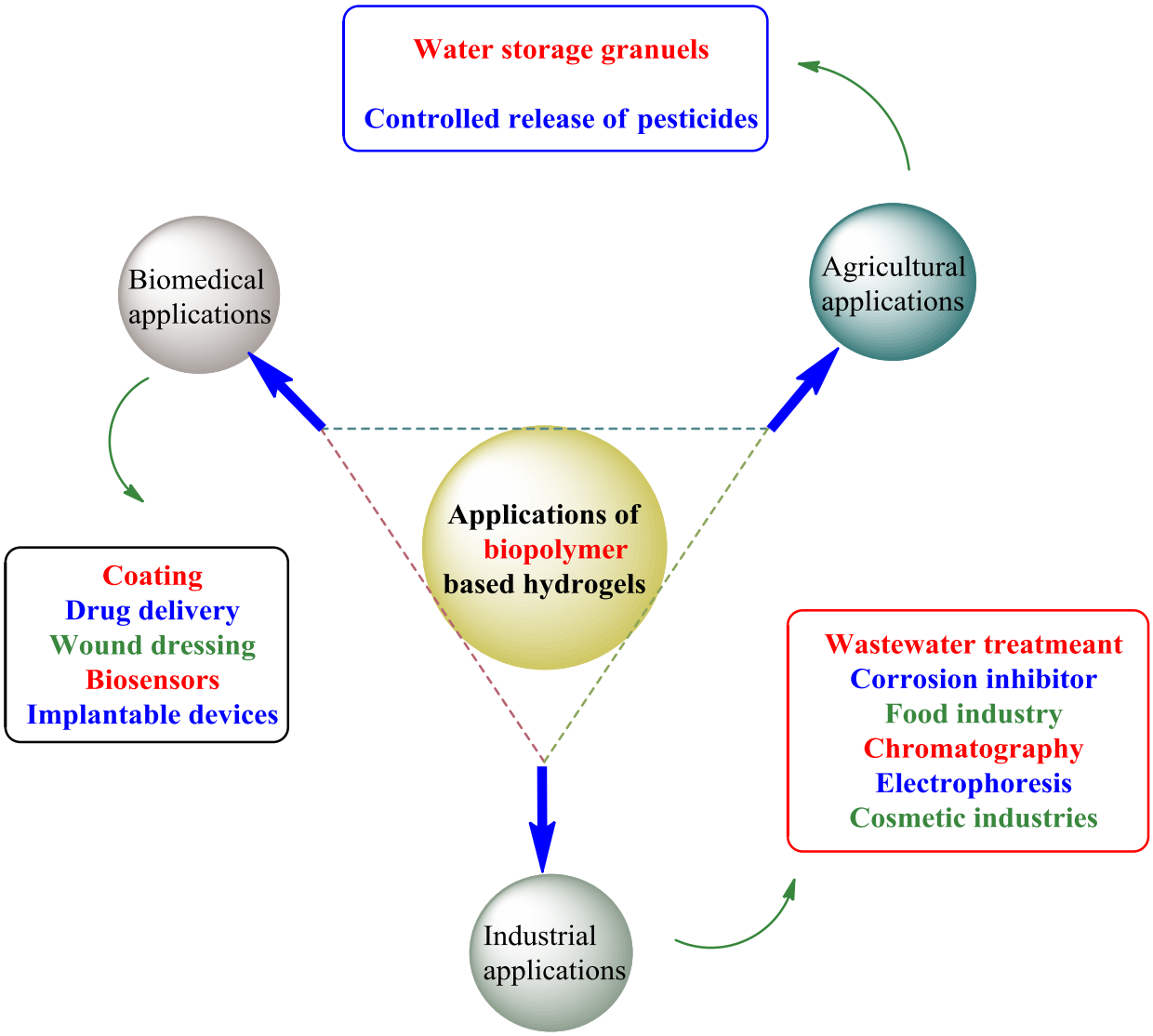


Figure 1. Applications of biopolymer based hydrogels.

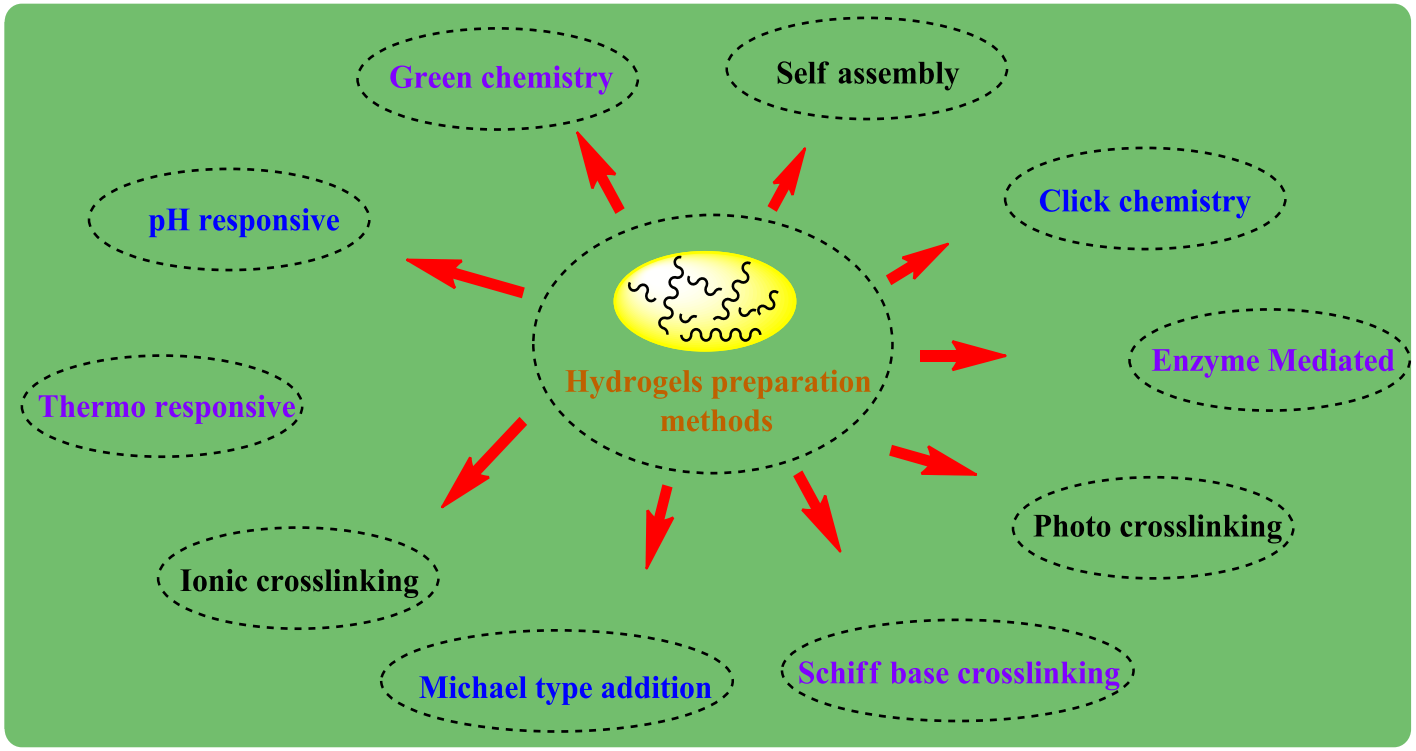


Figure 2. Different paths to synthesis of hydrogels.

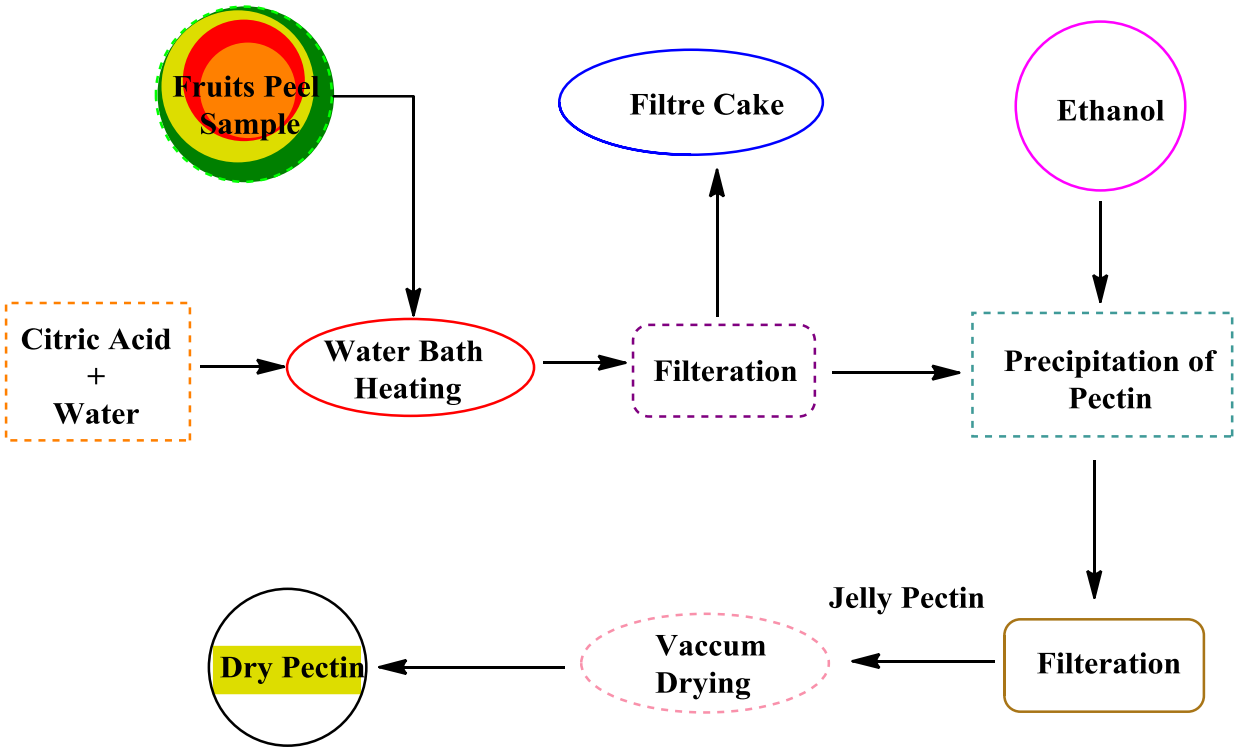


Figure 3. Extraction of pectin from bio-waste (fruits peels like orange, apple, mango etc.) materials.

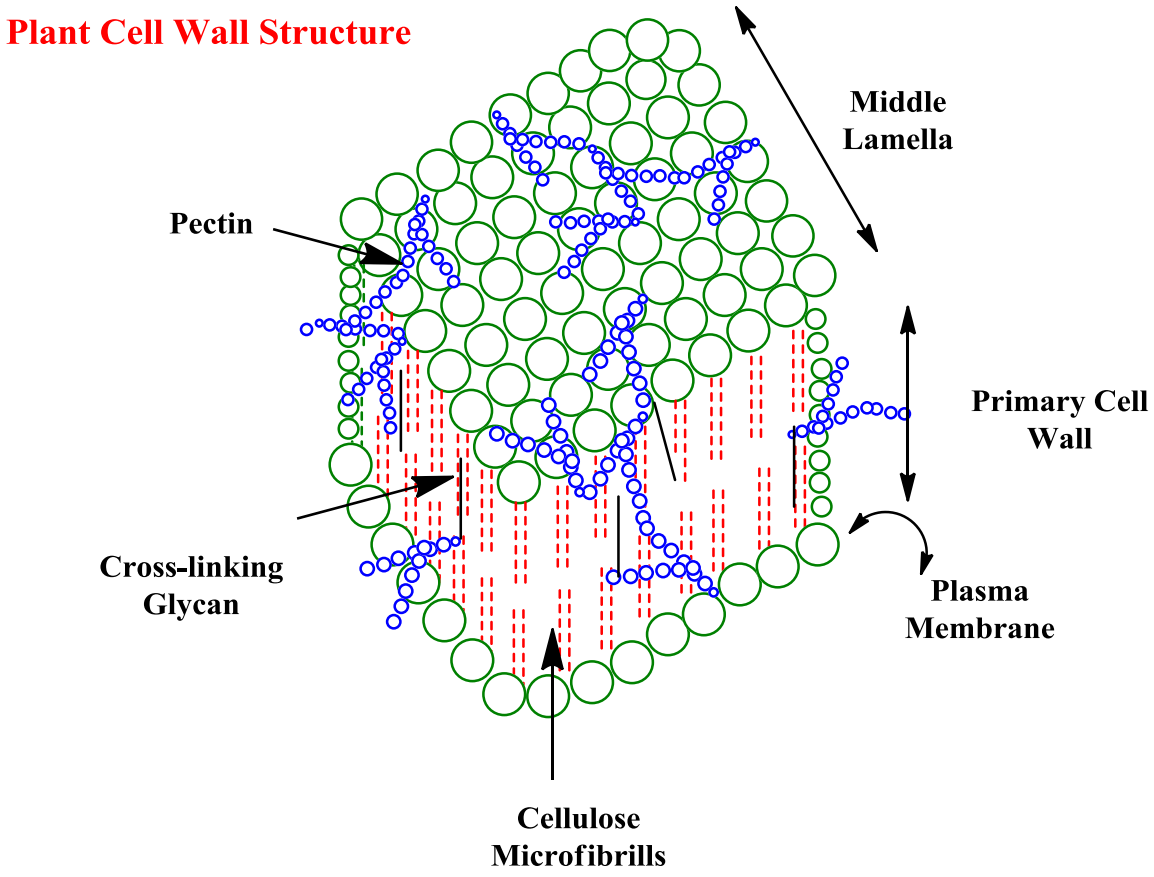


Figure 4. Pictorial presentation of simple structure of the plants cell wall. Adopted from (Lodish et al., 2008).

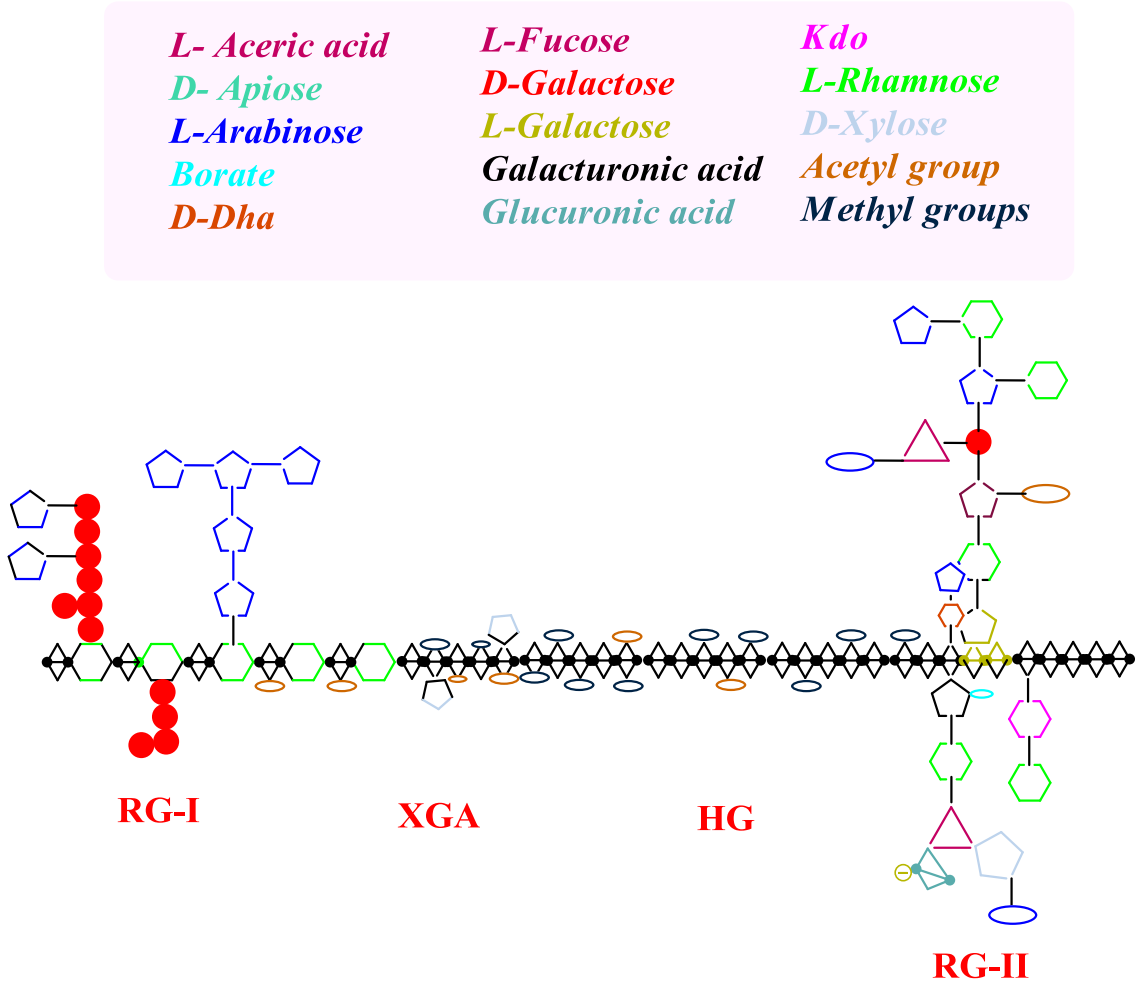


Figure 5. Four different pectic poly-saccharides homo-galacturonan, xylogalacturonan, rhamnogalacturonan Iand rhamnogalacturonan II. Adopted from (Mohnen, 2008a).

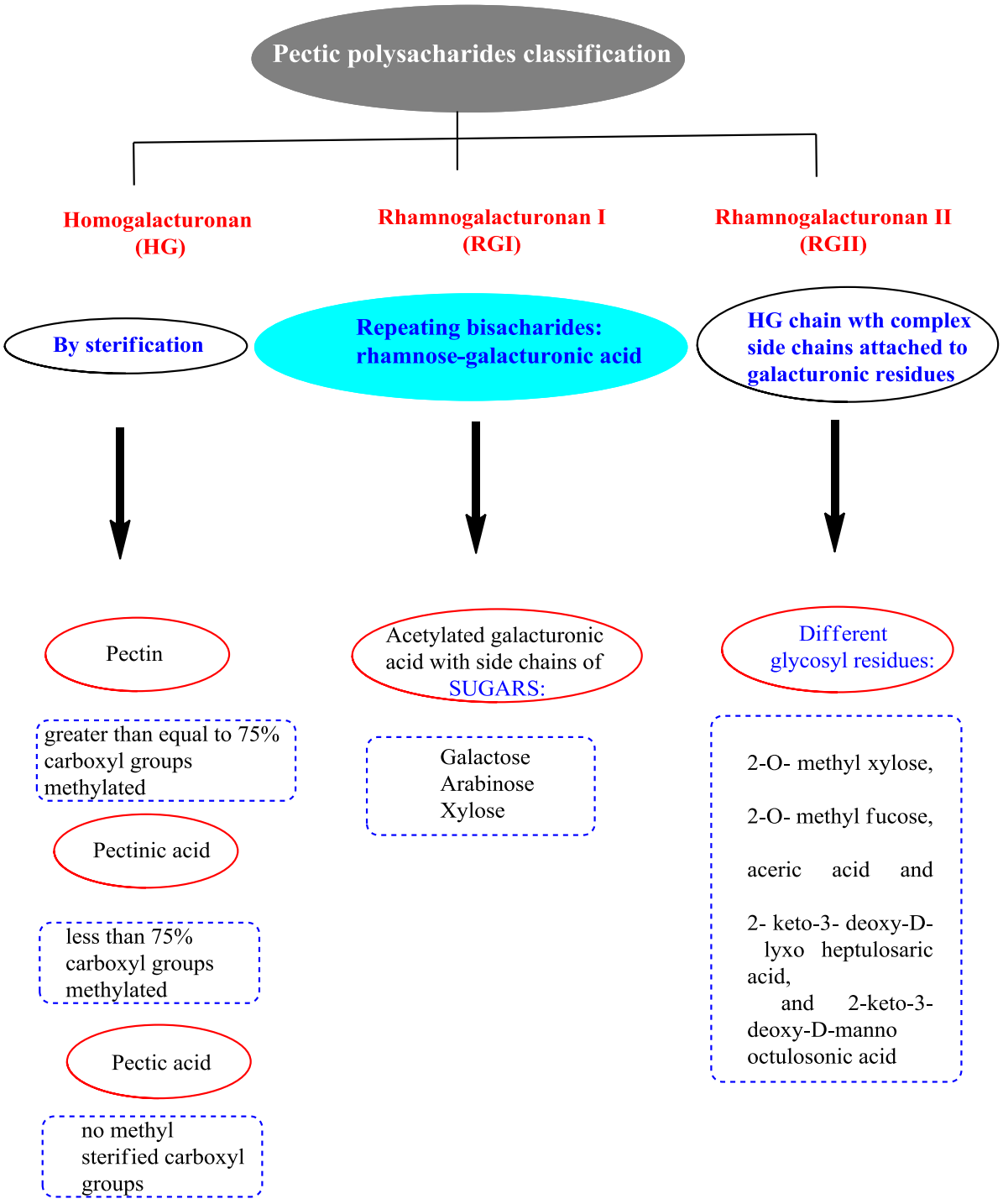


Figure 6. Three different kinds of pectic polysaccharides on the bases of D-galacturonic acid. Adopted from (Valdés García et al., 2015).

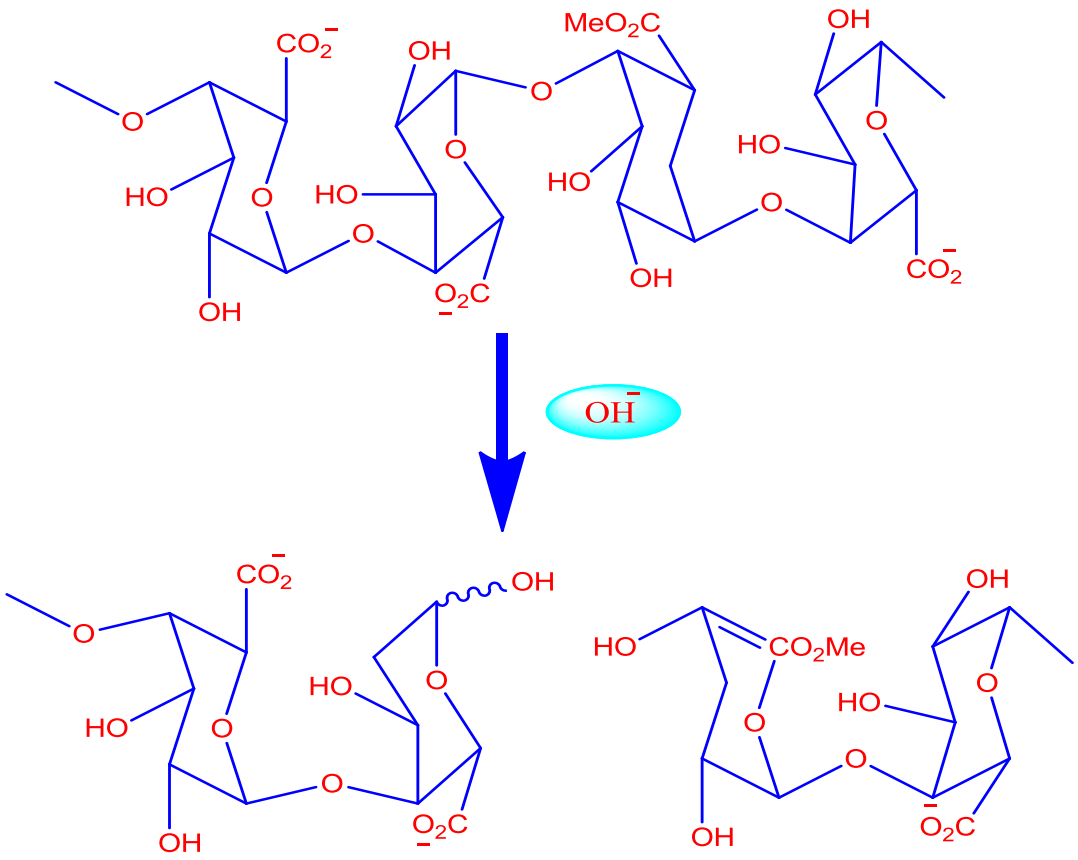


Figure 7. Arrangement of a pectenic acid of DE (degree of esterification) with the alkaline de-polymerization. Adopted from (BeMiller, 1986a).

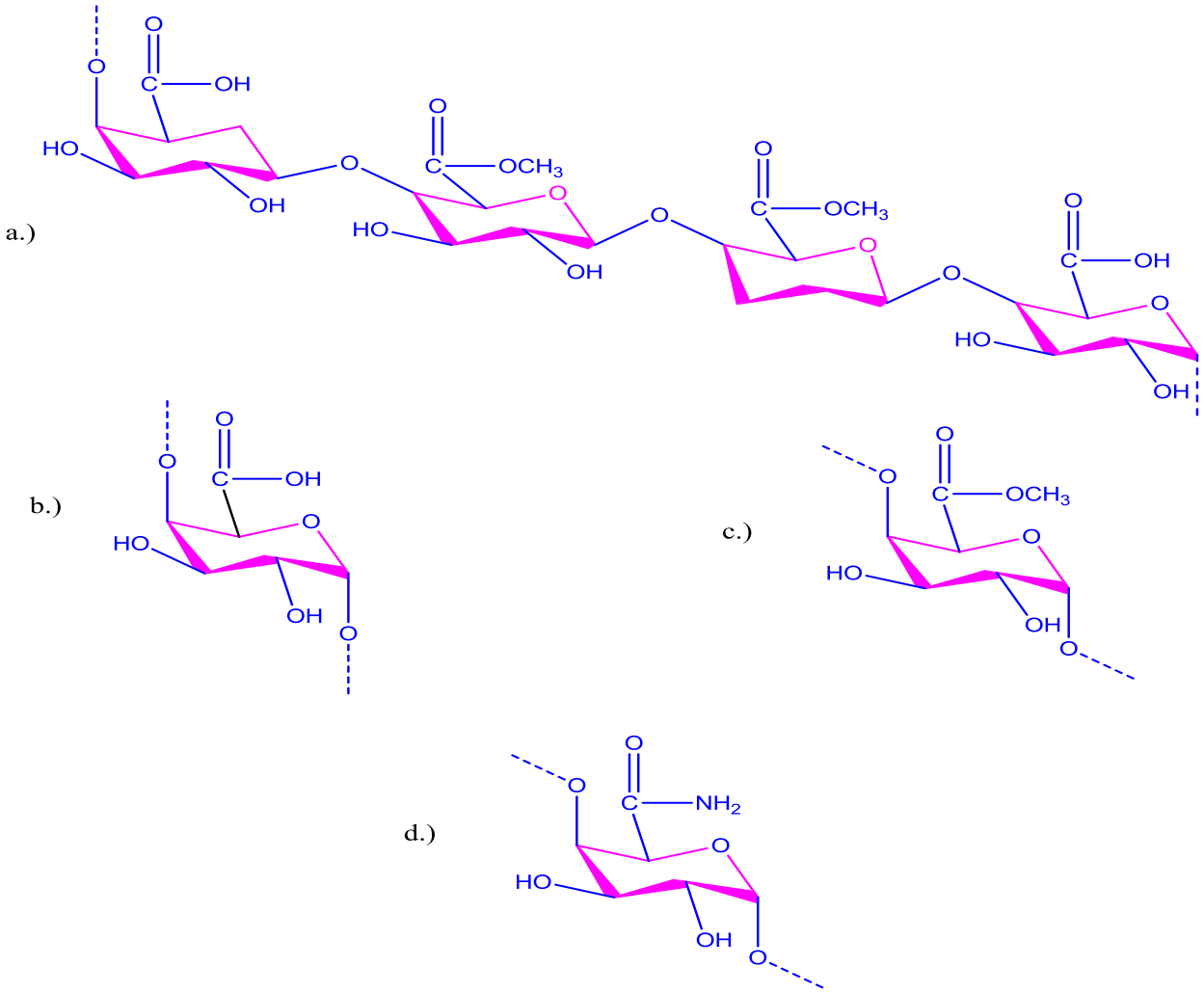


Figure 8. (a) Repeating unit of functional group in the form of pectin chemical structure, occurrence of (b) carboxylic group, (c) ester group and (d) amide group in pectin chain. Adopted from (Sriamornsak, 2003).

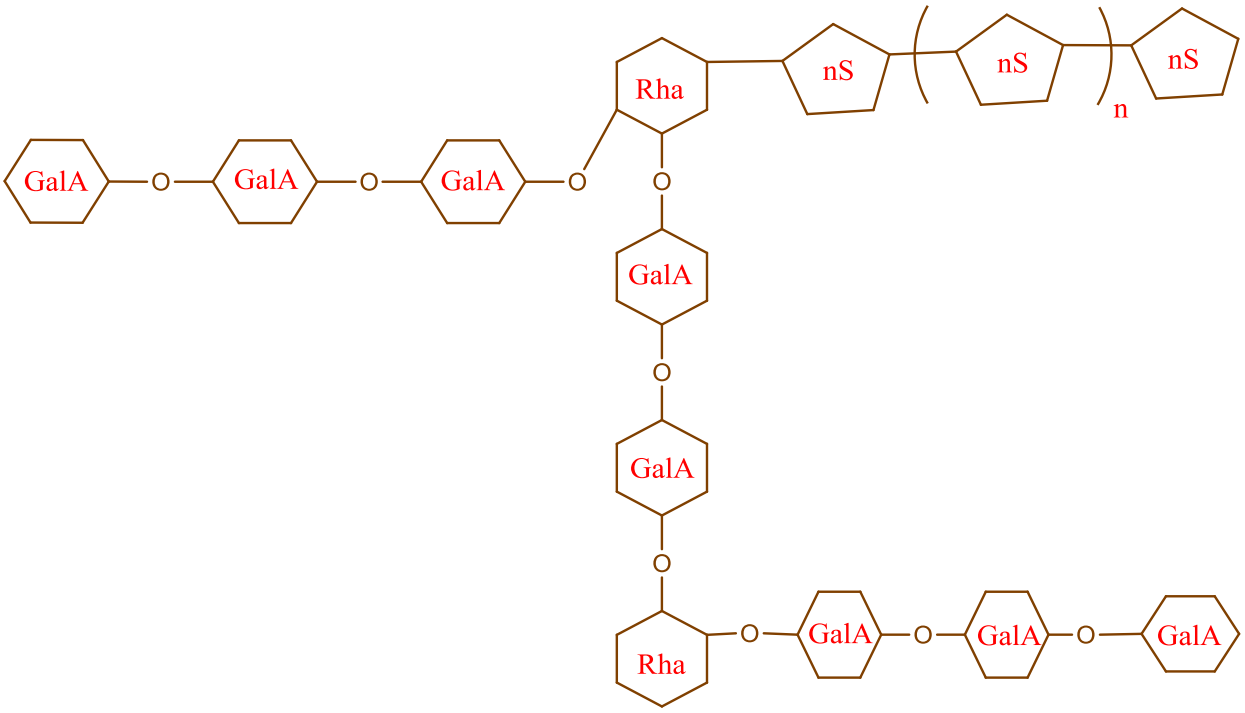


Figure 9. Rhamnose insertion cause occurrence of galacturonic acid chain (where nS shows the occurrence of neutral sugar) Adopted from (Sriamornsak, 2003, 2002).

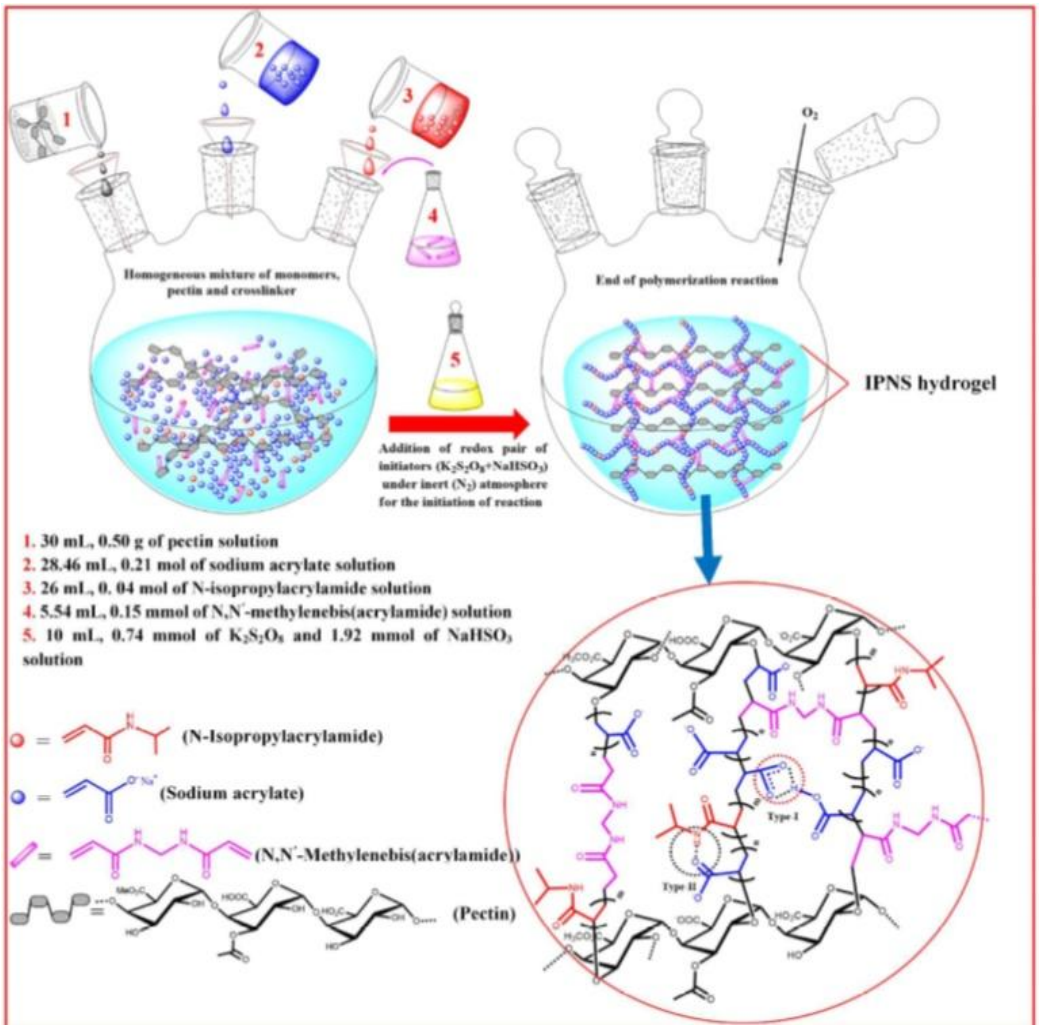


Figure 10. Schematic reaction procedure for synthesis of pectin-g-(sodium acrylate-co-N-iso-propyl acrylamide) hydrogel (Singha et al., 2017). Reprinted with permission from (Singha et al., 2017). Copyright 2017 Royal Society of Chemistry.

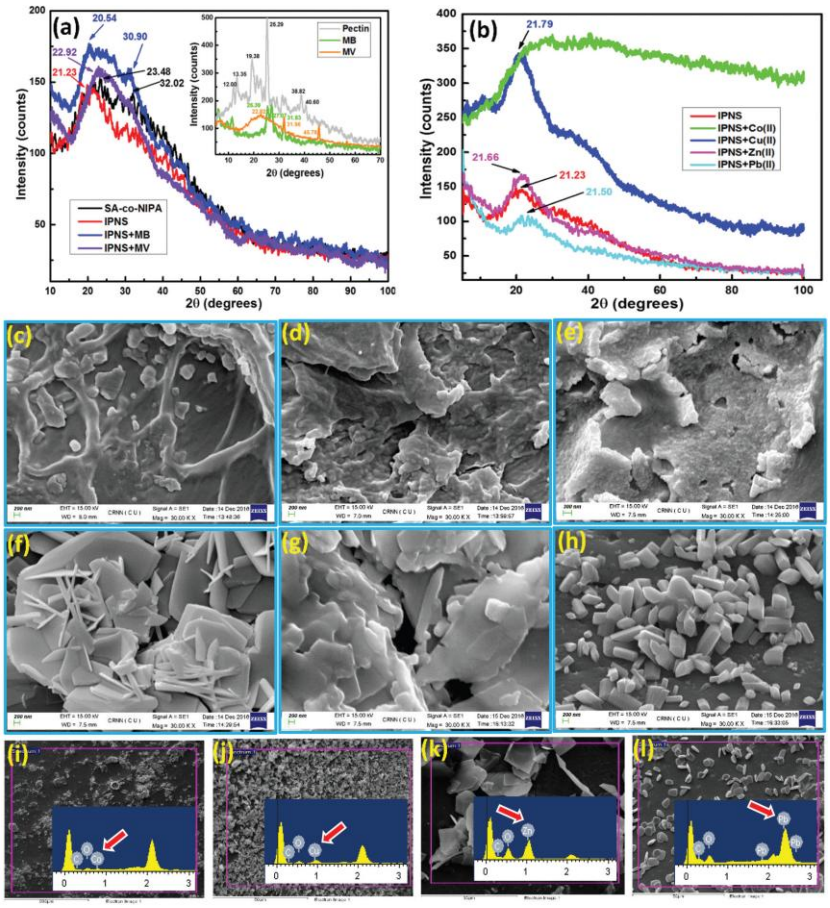


Figure 11. XRD spectra of (a) copolymer, interpenetrating polymer network superadsorbent (IPNS) and methylene blue/methyl violet loaded IPNS, (inset of a) pectin, methylene blue(MB) and methyl violet(MV), (b) Co(II), Cu(II), Zn(II) and Pb(II) loaded IPNS and SEM images of (c) sodium acrylate-co-N-iso-propylacylamide (SA-co-NIPA), (d) interpenetrating polymer network superadsorbent (IPNS) and SEM/respective EDX of (e)/(i) Co(II), (f)/(j) Cu(II), (g)/(k) Zn(II) and (h)/(l) Pb(II) loaded IPNS (Singha et al., 2017). Reprinted with permission from(Singha et al., 2017). Copyright 2017 Royal Society of Chemistry.

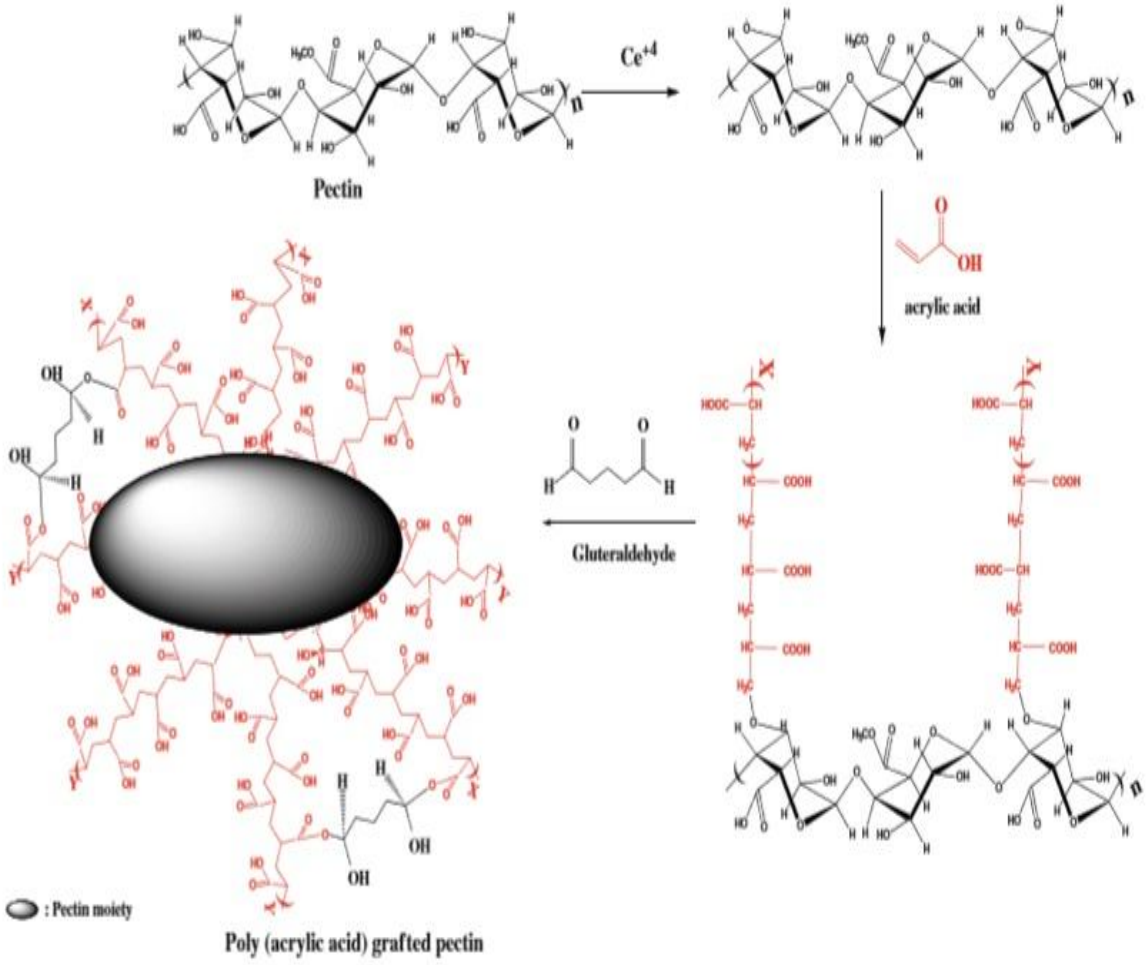


Figure 12. Synthesis of acrylic grafted pectin hydrogel by using acrylic acid (AA, 98%) as a monomer and glutar-aldehyde (GA) as a cross-linker (Fares et al., 2011). Reprinted with permission from (Fares et al., 2011). Copyright 2011 Springer.

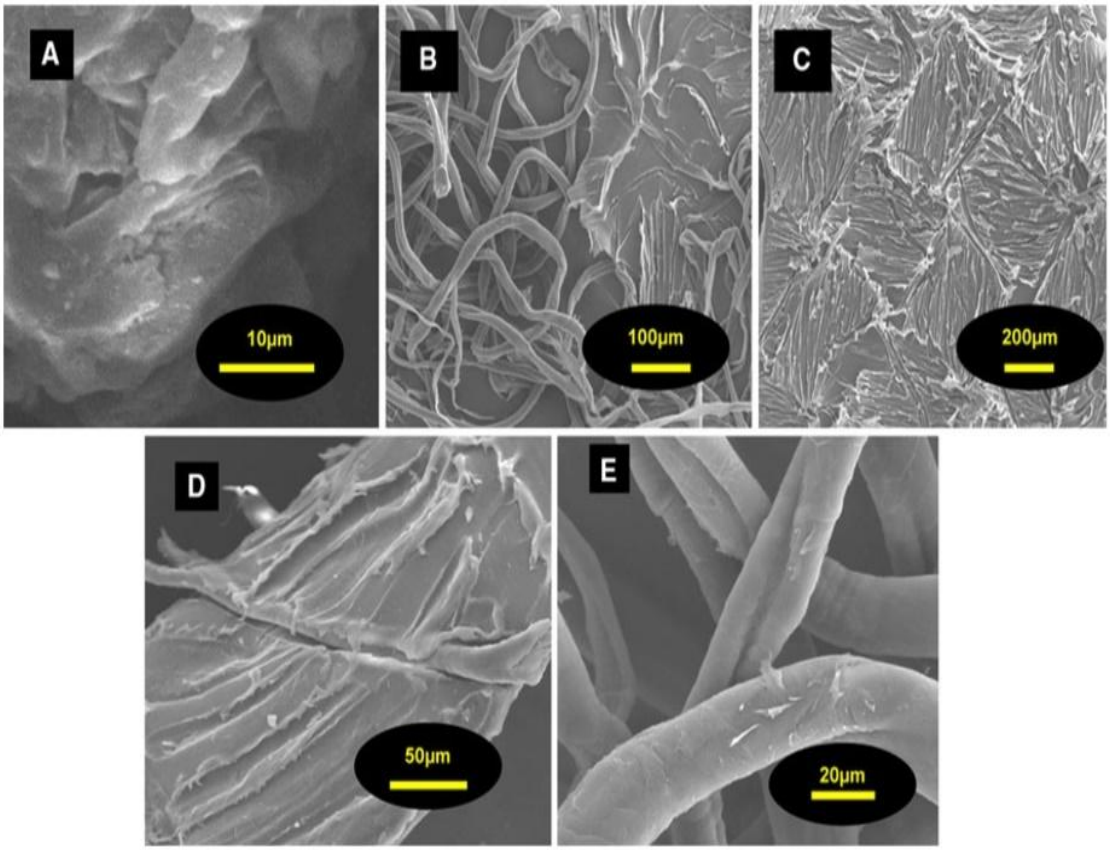


Figure 13. SEM morphology of (a) pure pectin hydrogel and (b, c, d and e) acrylic grafted pectin hydrogel (Fares et al., 2011). Reprinted with permission from (Fares et al., 2011). Copyright 2011 Springer.

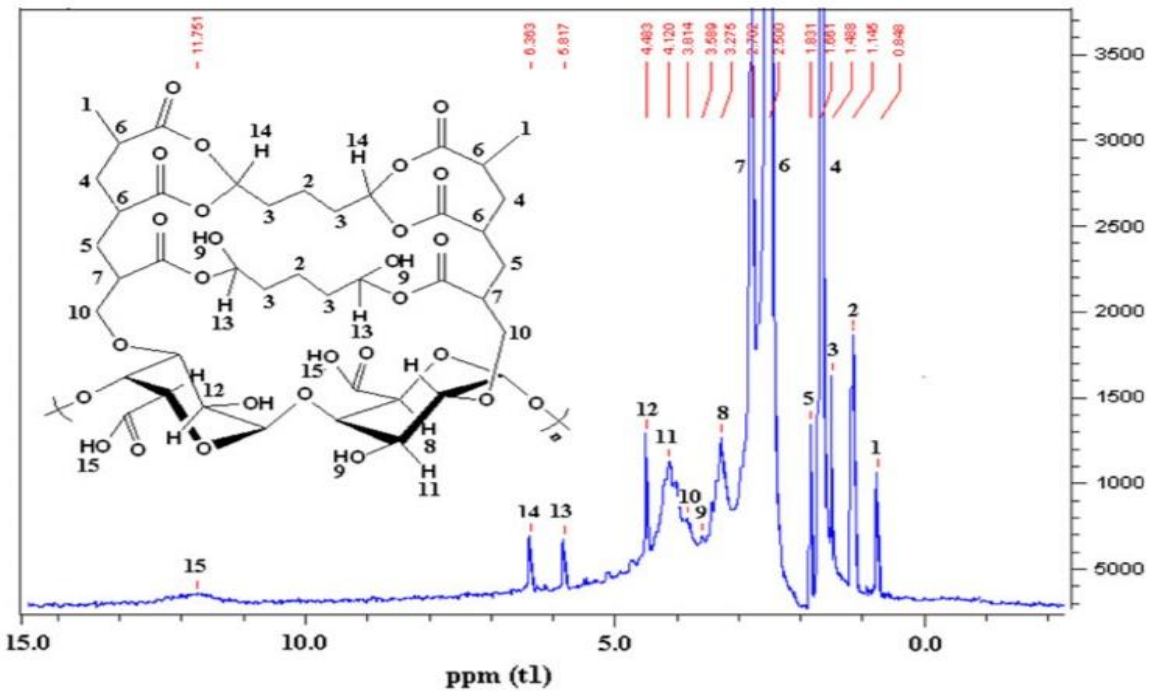


Figure 14. ^{1}H-NMR for acrylic grafted pectin hydrogel (Fares et al., 2011). Reprinted with permission from (Fares et al., 2011). Copyright 2011 Springer.

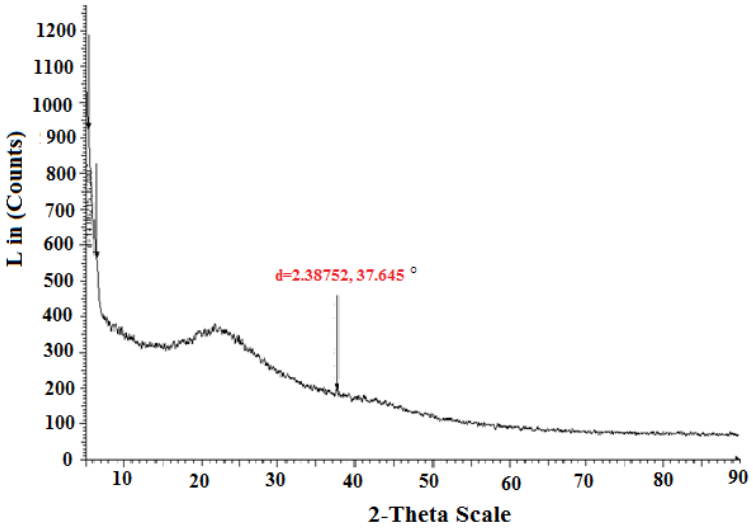


Figure 15. XRD of pectin based quaternary amino anion exchanger (Pc-QAE) material (Naushad et al., 2018). Reprinted with permission from (Naushad et al., 2018). Copyright 2018 Elsevier.

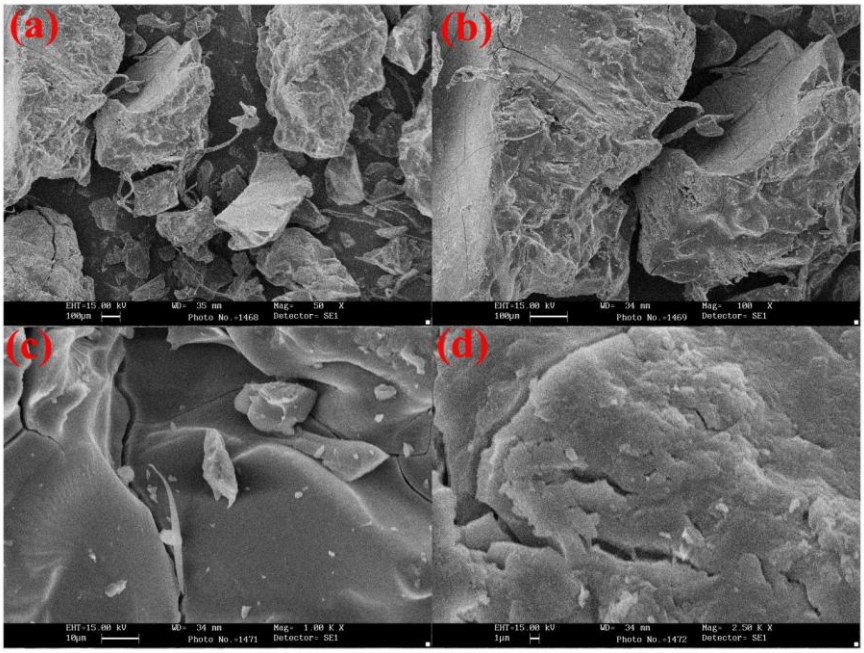


Figure 16. SEM images of pectin based quaternary amino anion exchanger (Pc-QAE) material at different magnification (Naushad et al., 2018). Reprinted with permission from (Naushad et al., 2018). Copyright 2018 Elsevier.

Table 1. Sol–gel (hydrosol–hydrogel) transition in chemical/organic and physical hydrogels.

Physical hydrogels	Chemical hydrogels
• Hydrophobic relationship: iso-propyl units in poly (N-isopropyl acrylamide); methyl units in methyl cellulose; propylene oxide obstructs in (ethylene oxide)–(propylene oxide)–(ethylene oxide) terpolymers. • Ion–polymer complexation: acrylic-based hydrogel activated with Ca, Al, Fe; Na-alginate activated with Cl and Al; polyvinyl alcohol activated with borax. • Polymer–polymer complexe formation: chitosan & alginate; gelatine& gum Arabic. • Chain summation; hydro-colloids heat treatment in water. • Hydrogen bonding: polyvinyl alcohol/polyvinyl alcohol chains bond; polyacrylic acid/polyacrylamide chains bond.	• Covalent cross-linking via olefinic cross-linkers having unsaturated bonds or sensitive functional groups. • Simultaneous polymerization & cross-linking: acrylic acid cross-linked via methylene; bis-acrylamide ethylene via glycol di-acrylate, ethylene glycol via di-methacrylate, polyethylene glycol via di-methacrylate. • Post-polymerization chemical cross-linking: Acrylic-based hydrogel, cross-linked via glycerin; glutaraldehyde cross-linked via gelatin; polyvinyl alcohol crosslinked via an aldehyde.

Table 2. Hydrogels responsive to alteration in environmental factors.

Hydrogels responsive to:		
pH	**Temperature**	**Liquid composition**
• In that case when hydrogels are ionic. • As increase in pH value • The swelling capacity increases in the anionic hydrogel having carboxyl groups like poly-sodium alginate. • The swelling capacity decreases in the cationic hydrogel having amino group like acrylate (dimethyl aminoethyl) and chitosan	• (In that case when hydrogels can form chain aggregation and can also form hydrophobic association) • as increase in temperature • in cellulose and in their derivatives, (like N-isopropyl Acrylamide and some cellulose based polymers) solubility decreases. • in hydro-colloids (like agar-agar and gelatin) solvability increases	• (In that case when the non-ionic and salts are contain around the hydrogels environment) • as alterations in swelling medium (either water or any aqueous medium) • in ionic hydrogels (like poly-potassium-acrylate) the swelling capacity decreases instantly with increase concentration value of non-solvent and salts • in non-ionic hydrogels (like polyvinyl alcohol) swelling capacity decreases moderately.

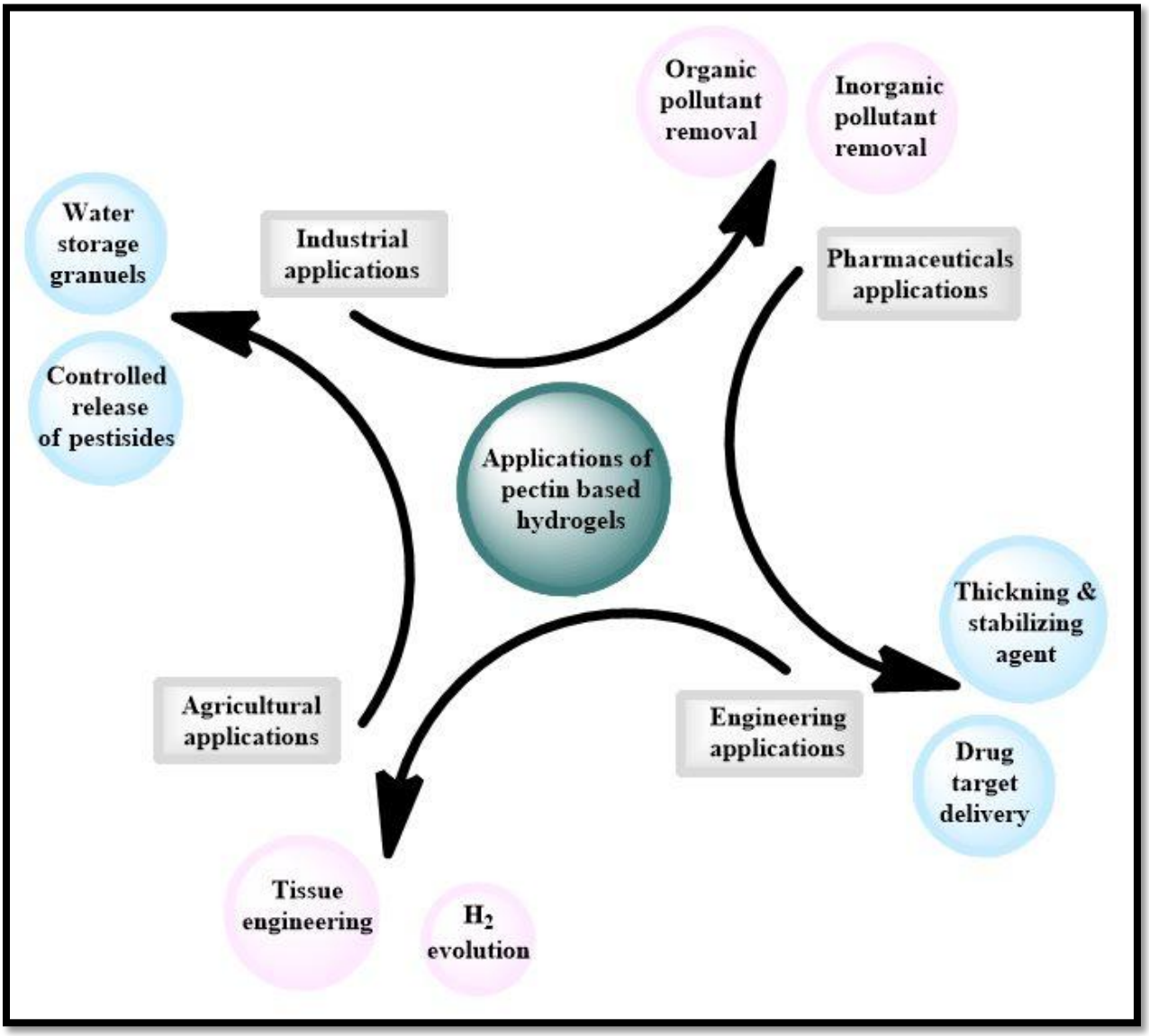
Table 3. Extraction of various bio-waste materials as pectin.

Sr. No.	Extraction of bio-waste material as pectin	References
1.	Citrus Limetta	(Garg, 2017)
2.	Orange waste	(Lessa et al., 2017a)
3.	Mango peels	(Banerjee et al., 2016)
4.	Pineapple peel	(Dai and Huang, 2016)
5.	Pineapple and Banana waste	(Yapo, 2009)
6.	Orange waste	(Biswas et al., 2007)

Table 4. Various pectin based hydrogels used for waste-water treatment.

Sr.No.	Pectin Based hydrogels	Pollutants	References
1.	Pectin-g-sodiumAcrylate-co-N-iso-propyl acrylamide hydrogel	Methylene blue & Methyl violet.	(Singha et al., 2017)
2.	Pectin based quaternary amino anion exchanger	Phosphate anions	(Naushad et al., 2018)
3.	Pectin/cellulose microfibers gel beads	Cd^{2+}, Cu^{2+} and Fe^{2+}	(Lessa et al., 2017b)
4.	Pectin/poly(acrylamide-*co*-acrylamidoglycolic acid) pH sensitive semi-IPN hydrogels	Ni^{2+}, Cu^{2+} , Co^{2+}	(Reddy et al., 2016)
5.	Acrylic grafted pectin hydrogel	Cd^{2+}	(Fares et al., 2011)
6.	Methacrylate-Pectin-co-Acrylamide-co-acrylic hydrogel	Cu^{2+}	(Guilherme et al., 2010)
7.	Iron-loaded pectin based hydrogel	As(V)	(Kumar et al., 2009)
8.	(i) Pectin-cl-poly-Acrylamide hydrogel (ii) Pectin-cl-poly-N-isopropyl-Acrylamide hydrogel (iii)Pectin-cl-poly-2-Acrylamido-2-methyl-1-propane-sulphoic hydrogel.	Cr^{6+}, Cu^{2+} and Fe^{2+}	(Chauhan et al., 2007)

Graphical Abstract



Highlights

- Hydrogel is used as sustainable noble material.
- Structure and properties of pectin are described.
- Pectin is produced from bio-waste materials.
- Pectin based hydrogels are used in water purification.
- The mechanical strength of pectin based hydrogel can be improved by incorporation of nanoparticles.

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Progress in pectin based hydrogels for water purification: trends and challenges

Thakur, Sourbh

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